SUMMARY OF THE QUALITY SYSTEMS COMMITTEE MEETING AUGUST 17, 2000

The Quality Systems (QS) Committee of the National Environmental Laboratory Accreditation Conference (NELAC) met by teleconference on August 17, 2000, from 1 - 3 p.m. Eastern Daylight Time (EDT). The meeting was led by its chair, Mr. Scott Siders of the Illinois Environmental Protection Agency. A list of action items is given in Attachment A. A list of participants is given in Attachment B. The homework table is provided in Attachment C. *The purpose of the meeting was organize the committee following the Sixth NELAC Annual Meeting (NELAC VI) and to initiate committee work leading up to the Sixth NELAC Interim Meeting (NELAC VIi) scheduled to begin October 31, 2000.*

INTRODUCTION

Mr. Siders reviewed the agenda for the meeting and established goals and schedules to be accomplished before the NELAC VIi meeting beginning on October 31, 2000 in Las Vegas NV. No new comments have been received on Chapter 5 since the 7/20/00 teleconference. Some of the committee members did not get e-mails related to the meeting. Mr. Siders will update the mailing list and send a test message to all members to ensure addresses are correct.

TOPICS OF DISCUSSION

ISO 17025

The committee is considering revisions to Chapter 5 needed to integrate the International Standards Organization (ISO) 17025, "General Requirements for the Competence of Testing and Calibration Laboratories." The committee discussed a possible approach to be taken for the integration. The committee feels that considerable work will be needed to meet this new standard, and that no final proposed language will be available at the NELAC Interim Meeting. The committee does want to have some discussion materials to present at the NELAC Interim Meeting. The committee is working on a table that will compare NELAC Chapter 5 to the ISO 17025 standard. Mr. Siders intends to discuss this issue more with Dr. Fred Siegelman of the U.S. Environmental Protection Agency (EPA).

Mr. Siders informed the committee that EPA legal staff is discussing the present copyright fee issues with the American National Standards Institute (ANSI) and ISO.

Microbiology Testing Subcommittee

Ms. Marty Casstevens reported that progress in addressing the microbiology sections of Chapter 5 has been good. The subcommittee is attempting to incorporate appropriate references where needed for some of the language in the section. The subcommittee is reviewing language for positive, negative and sterility controls and duplicate samples. A requirement for participation in proficiency testing twice a year for each analyte is a problem for some laboratories. Ms. Casstevens will discuss this issue on

frequency of testing with Ms. Barbara Burmeister of the Proficiency Testing Committee. The subcommittee is also addressing requirements for culture maintenance which will be practical for small laboratories . Language in Chapter 5 addressing method evaluation may be unnecessary since methods for microbiological monitoring are usually prescribed by regulations. The subcommittee has conference calls scheduled for 8/30/00 and 9/7/00. All revisions to the section will be sent to the chair and to the contractor no later than 9/8/00.

Environmental Laboratory Advisory Board (ELAB) Comments on D.1

Mr. Siders and Mr. Charlie Hooper will review these comments and bring proposed language to the committee at the 8/31/00 meeting. The ELAB recommendations are given in Attachment D of these minutes. Mr. Siders said they will primarily focus on the ELAB proposed language concerning method blanks, surrogates and matrix spikes (MS) and matrix spike duplicates (MSDs). Mr. Siders indicated that at present he favors the proposed language submitted by ELAB.

Toxicity Testing Subcommittee

Dr. Peter De Lisle discussed revised language for dilution water. EPA regulations are not definite about requirements for dilution water and there is concern that laboratories may miss proficiency test samples if they do not have requirements for testing dilution water.

DoD Comments

Comments from the Department of Defense (DoD) which were tabled while the committee dealt with more urgent topics must now be addressed. Assignments for various sections of Chapter 5 were made by the chair. Sections 5.0 to 5.16 will be addressed by Dr. George Kulasingham, Mr. Jeff Neilsen, and Mr. David Mendenhall. Mr. Siders and Mr. Charlie Hooper will review Section D.1. Dr. De Lisle will review Section D.2, Mr. Cliff Glowacki will review D.5 and the Microbiology Subcommittee will review the D.3 comments.

Asbestos Testing Appendix and Subcommittee

There is no report for this subcommittee since Dr. Kulasingham was on travel and not able to participate in the conference call.

Deadlines for Committee Revisions for NELAC VIi

All revisions to be discussed at NELAC VIi must be completed and forwarded to the contractor by September 8, 2000. This deadline will allow them to make the needed revisions to Chapter 5. These changes will be reviewed and discussed at the September 14, 2000 Quality Systems teleconference.

Next Meeting

The next meeting of this committee is scheduled for August 31, 2000 at 1 p.m. EDT.

Attachment A

ACTION ITEMS
QUALITY SYSTEMS COMMITTEE
JULY 20, 2000

Item No.	Action Item	Date to be Completed
1	ISO 17026 subcommittee: Update on progress of copyright discussions on ISO 17025, Ms. Jackie Sample & Dr.Siegelman (co-chairs): Ms. Marlene Moore, Ray Frederici, Scott Siders, Carl Kircher are members.	8/31/00
2	Microbiology Testing Subcommitee: Revisions to Section on Microbiology to Mr. Siders and RTI following 9/7/00 teleconference, Ms. Casstevens (chair)	9/8/00
3	DoD comments reviewed and discussed prior at next QS teleconference on 8/31/00.	8/31/00
4	All proposed revisions to Chapter 5 forwarded to contractor.	9/8/00

Attachment B

PARTICIPANTS
QUALITY SYSTEMS COMMITTEE
AUGUST 17, 2000

Name	Affiliation	Phone Numbers
Mr. Scott D. Siders Chair	IL Environmental Protection Agency	T: 217-785-5163 F: 217-524-0944 E: epa6113@epa.state.il.us
Ms. Martha Casstevens	Froehling and Robertson	T: 804-264-2701 F: 804-264-0782 E: mcasstevens@fandr.com
Dr. Peter Delisle	Coastal Bioanalysts	T: 804-694-8285 F: 804-695-1129 E: pdelisle@coastalbio.com
Mr. Raymond J. Frederici (absent)	Severn Trent Laboratories	T: 708-534-5200 F: 708-534-5211 E: rfrederici@stl-inc.com
Mr. Clifford R. Glowacki	Technikon	T: 916-929-8001 F: 916-929-8020 E: cglowacki@cerp-aiger.org
Mr. Charlie Hooper	USEPA	T: 706-355-8838 F: 706-355-8803 E: hooper.charles@epa.gov
Dr. George Kulasingam (Joel Ondo on behalf of GK)	CA Department of Health — ELAB	T: 510-540-2800 F: 510-849-5106 E: gkulasin@dhs.ca.gov
Ms. Sylvia S. Labie (absent)	Florida Department of Environmental Protection	T: 850-488-2796 F: 850-922-4614 E: labie_s@dep.state.fl.us
Mr. David Mendenhall	UT Department of Health	T: 801-584-8470 F: 801-584-8501 E: dmendenh@doh.state.ut.us
Mr. Jeff Nielsen	City of Tallahassee Water Quality Division	T: 850-891-1232 F: 850-891-1062 E: nielsenj@mail.ci.tlh.fl.us
Dr. Fred Siegelman (absent)	USEPA, OEI	T: 202-564-5173 F: 202-565-2441 E: siegelman.frederic@epamail.epa.gov
Mr. Michael E.Beard (Contractor Support)	Research Triangle Institute	T: 919-541-6489 F: 828-628-7386 E: mebeard@rti.org

Attachment C

Comments to QS Committee
Log & Status Table 4/23/00

From (Organization)	From (Person)	Date Recieved	Commentor Notified of Receipt (Y/N)	Format OK? (Y/N) & WORDPERFECT OR WORD OR RICH TEXT	Number/Letter Assigned	Due Date	Compl. Date
15 Wi DNR	A. Sotomayor	4/1/99	Y	Y	wisc_1 **One**	~~6/2~~ **9/22/99**	10/18/99
16 Navy	Elsie Munsell	4/1/99	Y	Y	Navy_1.wpd **Two**	6/2 **9/22/99** **9/22/99**	6/17/99
17 Arizona	George Avery	4/29/99	Y	N	not electronic **Three**	~~5/26~~ **9/22/99**	9/22/99 12/7/99
South Carolina	Carol Smith	6/24/99	N	N (hardcopy)	**Four**	**10/15/99**	11/26.99 12/7/99
Fl Dept. of Health	Steve Arms	7/14/99	Y	Y(File not avail)	**Five**	**10/15/99**	10/15/99
Hillsboroght Co. Water Dept.	Steve Axelrod	8/10/99	Y	N(File not avail)	**Six**	**10/15/99**	10/15/99
DOD	Jackie Sample	8/24/99	Y	N (Yes Email)	**Seven**	**10/15/99**	11/16/99
Lehigh Co. Authority	Donna Farber	9/2/99	Y	N (Yes Email)	**Eight**	**10/15/99**	1/7/00
W. Coast Analytical Service, Inc.	Jack Northington	9/1/99	Y	N (Yes Email)	**Nine**	**10/15/99**	12/7/99
Catalyst	Jerry Parr	9/7/99	Y	N (Yes Email) Gen. Questions	**Ten**	**10/15/99**	1/7/00
New Hampshire	Charles Dyer	?	N	Y(file not avail)	**Eleven**	**!0/1/99**	10/15/99
CA ELAB	Steve Boggs	9/22/99	Y	Y	**Twelve**	**10/15/99**	12/7/99
Eastman Kodak	Don Zahniser	9/22/99	Y	Y	**Thirteen**	**10/15/99**	1/7/00 outstanding items in 1/7/00 parking lot Completed on 4/14/00
Test America	Paul Juno	9/22/99	Y	Y	**Fourteen**	**10/15/99**	1/7/00 up to 5.12.3.3 and completed 4/14/00
WI DNR	A. Sotomayor	9/25/99	Y	Y	**Fifteen**	**10/15/99**	12/7/99
SAFETY-KLEEN CORP	VINCENT DONNDELINGER	1/3/00	Y	Y/N	A	2/9/00	4/14/00
CA-DHS	JANE JENSEN	1/3/00	Y	Y/N	B	3/1/00	2/16/00 & 3/15/00

Attachment C

CA-DHS	JUNE KANI	1/3/00	Y	Y/N	C	2/9/00	1st 1/3 2/9/00 and last 2/3 4/14/00
USEPA - REGION 4	CHARLIE HOOPER	12/20/99	Y	Y/N	D	2/9/00	2/23 & 36/00
DAVIS & FLOYD ENG.	CARL BURRELL	1/5/00	Y	Y/N	E	2/9/00	4/14/00
QC-INC	70720 HEIDI KRUEGER MARLENE MOORE	1/14/00	Y	Y/N	F	2/9/00	4/14/00
NY-SDH	KEN JACKSON	1/11/00 1/12/00	Y	Y/N	G	1/24/00	1/24/00
FIRST ENV	LORRIE FRANKLIN	12/3/99	Y	Y/N	H	2/9/00	1/24/00
Advanced Systems, Inc.	Marlene Moore	2/8/00	Y	Y	C1	3/6/00	3/6/00
PDC Labs, IL	Jeff Loews	3/6/00	Y	Y/N	C2		3/21/00
Field Activities Committee	Bart Simmons	3/2/00	Y	Y/N	C3		3/21/00
ELAB	J. Wilson Hershey	2/28/00	Y	Y/N	C3		3/13/00 and 3/21/00 and 4/14 and 4/17
UOSA	Bill Nivens	3/15/00	Y	Y/N	C4		3/15/00
Fl	Steve Arms	3/10/00	Y	Y	C5		3/21/00
Hampton Roads Sanitary Authroity	Stancie Calacsan	1/24/00	Y	Y/N	I		4/19/00
California Health Dept.	June Kani	2/10/00 and 4/14/00	Y	Y	J		4/19/00
WI	Laura Trans	2/25/00	Y	Y	K		4/19/00
Severn Trent Labs STL	Deb Loring	3/16/00	y	Y/N	l		4/19/00
KS	Aurora Shields	2/29/00	Y	Y	M		3/9/00
FL DEP	Silky Labie	3/12/00	Y	Y	N		4/17 & 4/19
CA Health Dept.	Jane Jensen	3/12/00	Y	Y	O	**NELAC 6**	**NELAC 6**
PA DEP	Michael DePalma	3/30/00	Y	Y	P		4/19/00
Envir. Quality Management	Larry Jackson	4/4/00	Y	Y	Q	**NELAC 6**	**NELAC 6**
East Coast NELAC Assessors	Marlene Moore	3/31/00	Y	N	R	**NELAC 6**	**NELAC 6**

Note: The comments will be discussed during QS Committee meetings and the QS consensus comments will be included with the committee minutes. The final version of the tables/sections of tables will be forwarded by the lead after the Committee meeting so that it can be attached to the minutes. As the final response will be the consensus of the QS committee, the name of the group leader/s will not be included in the minutes/web posting.

Attachment D

MEMORANDUM

To: Jim Pearson, Chair of the NELAC Board of Directors

CC: Jeanne Hankins, NELAP Executive Director
Joe Slayton, Chair, Quality Systems Committee

From: Environmental Laboratory Advisory Board

RE: Recommendations for Changes to Appendix D of Chapter 5 of the NELAC Standards

Date: May 11, 2000

The Environmental Laboratory Advisory Board (ELAB) strongly requests NELAC to consider revising Appendix D of Chapter 5 of the NELAC standards as summarized in the enclosed attachment. We would request these changes be voted on this year, with an immediate effective date.

ELAB believe the current language provides onerous requirements for laboratories, unnecessarily increasing the cost for environmental monitoring; is in conflict with several EPA regulations; perpetuates the confusion about the appropriate role of matrix quality control samples, and does not adequately describe an essential element for laboratory accreditation.

ELAB has formed a subcommittee for this issue, and offers the energy of this subcommittee over the next few months to work with the Quality Systems committee to resolve any differences prior to the July, 2000 Conference. The changes ELAB is proposing are only an interim measure; ELAB believes Appendix D needs a more thorough revision, using language in the enclosed attachments as a basis.

Attached is the suggested changes to Appendix D shown in revision/strikeout mode (Attachment 1), a white paper on this topic developed by the ELAB subcommittee (Attachment 2), and background supporting information on this topic published by EPA and the US Army Corps of Engineers (Attachment 3) which should be considered as the Quality Systems committee considers future revisions.

Attachment D

RECOMMENDATIONS FOR QUALITY CONTROL SAMPLES

Environmental Laboratory Advisory Board

May 11, 2000

DRAFT

Attachment D

Attachment 1

PROPOSED CHANGES TO APPENDIX D

Appendix D -ESSENTIAL QUALITY CONTROL REQUIREMENTS

The quality control protocols specified by the laboratory's method manual (5.10.1.2) shall be followed. The laboratory shall ensure that the essential standards outlined in Appendix D are incorporated into their method manuals and the Laboratory Quality Assurance Plan.

All quality control measures shall be assessed and evaluated on an on-going basis and quality control acceptance criteria shall be used to determine the validity of the data. The laboratory shall have procedures for the development of acceptance/rejection criteria where no method or regulatory criteria exists.

The requirements from the body of Chapter Five, e. g., 5.5.4, apply to all types of testing. The specific manner in which they are implemented is detailed in each of the sections of this Appendix, i. e., chemical testing, W. E. T. testing, microbiology testing, radiochemical testing and air testing.

D. 1 CHEMICAL TESTING

D. 1.1 Positive and Negative Controls

a) Negative Controls

1) Method Blanks ~~Shall be performed at a frequency of one per batch of samples per matrix type per sample extraction or preparation method. The results of this analysis shall be one of the QC measures to be used to assess batch acceptance. The source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem if~~

~~i) the blank contamination exceeds a concentration greater than 1/10 of the measured concentration of any sample in the associated sample batch or~~

~~ii) the blank contamination exceeds the concentration present in the samples and is greater than 1/10 of the specified regulatory limit.~~

Use – The method blank is used to assess whether the batch was subject to contamination during processing. The method blank is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures.

Frequency - shall be analyzed at a minimum of 1 per batch of 20 or less samples per matrix type per preparation test method. Where no preparation method exists (example, volatile organics, water) the batch is defined as environmental samples that are analyzed together with the same process and personnel, using the same lots of reagents, not to exceed 20 environmental samples.

Composition – A sample matrix that is similar to the batch of associated samples (when available), free from the analytes of interest

Acceptance Criteria - Each sample in the affected batch must be assessed against the following criteria to determine if the sample datum is acceptable. The source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem if:

the blank contamination exceeds the reporting limit, or the blank contamination exceeds the concentration present in the samples and is greater than 1/10 of the specified regulatory limit, whichever is greater;

if the blank contamination exceeds a concentration greater than 1/10 of the measured concentration of any sample in the associated sample batch or

or blank contamination otherwise affects the sample results, as per individual test method requirements.

Any sample associated with ~~the~~ a contaminated blank shall be reprocessed for analysis or the results reported with appropriate data qualifying codes.

b) Positive Controls

Attachment D

1) Laboratory Control Sample (LCS) -(QC Check Samples)-

Use - LCS is used to verify that the accuracy of the analytical process is within the expected performance of the method. The results of the LCS are compared to acceptance criteria to determine the validity of the associated sample data. Sample data generated in a batch with LCS results that fall outside the established acceptance criteria are judged to be generated during an "out-of-control" situation. These data are considered suspect and are repeated or reported with qualifiers.

Frequency – shall be analyzed at a minimum of 1 per batch of 20 or less samples per matrix type per preparation test method except for analytes for which spiking solutions are not available such as total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, odor, temperature, dissolved oxygen or turbidity. Where no preparation method exists (example, volatile organics, water) the batch is defined as environmental samples that are analyzed together with the same process and personnel, using the same lots of reagents, not to exceed 20 environmental samples.

Composition - If the test method does not specify the spiking compounds, the laboratory shall spike all reportable components in the LCS. In cases where the components interfere with accurate assessment (such as simultaneously spiking chlordane, toxaphene and PCBs in Test method 608), other related analytes may be substituted for the multi-component analytes. Where the test method has an extremely long list of components (such as Test method 8270 or 6010) or components are incompatible, a representative number (10%) of the listed components may be used to control the test method. The selected components of each spiking mix shall represent all chemistries, elution patterns and masses and shall include permit specified analytes and other client requested components. Spiking levels should conform to method requirements. In the event that methods do not specify spiking levels, the laboratory should choose a spiking level above the typical reporting limit and less than or equal to the mid-range of the calibration range.

Acceptance Criteria – The results of individual batch LCS are calculated as ~~in~~ percent recovery (%R):

$$\%R = \frac{\text{Observed Value}}{\text{True Value}} \times 100\%$$

The %R values are then compared to associated QC acceptance criteria. The LCS results are one of elements used to determine the validity of the data in the associated batch. Typically, acceptance criteria are taken from published EPA methods. Where no EPA criteria exist, or where the EPA limits do not reflect inter-laboratory performance, laboratory generated acceptance criteria should be established. Acceptance criteria for bias should be based on the mean recovery plus or minus three standard deviation units, from a minimum of twenty data points. Laboratory generated acceptance criteria should be periodically updated with continued use of the analytical method. Many published EPA methods do not contain recommended acceptance criteria for QC sample results. In these situations, 70 - 130% should be used as interim acceptance criteria for recoveries of spiked analytes, until in-house limits are developed.

Analytical data generated with LCS that fall within prescribed acceptance criteria are judged to be generated while the laboratory was in control. Data generated with LCS that fall outside the established acceptance criteria are judged to be generated during an "out-of-control" situation. These data are considered suspect and are repeated or reported with qualifiers.

~~Shall be analyzed at a minimum of 1 per batch of 20 or less samples per matrix type per sample extraction or preparation method except for analytes for which spiking solutions are not available such as total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, odor, temperature, dissolved oxygen or turbidity. The results of these samples shall be used to determine batch acceptance. NOTE: the matrix spike (see 2 below) may be used in place of this control as long as the acceptance criteria are as stringent as for the LCS.~~

Data Assessment Controls

The laboratory must document procedures for determining the effect of the sample matrix on method performance. These procedures involve the analyses of matrix specific QC samples and surrogate spikes. In general, these activities are designed to assess data quality and not judge laboratory performance.

Matrix Specific QC Samples include: Matrix Spike (MS), Matrix Spike Duplicate (MSD) and Matrix Duplicate (MD) Samples

Use – Matrix specific QC samples show the effect of the sample matrix on the accuracy and precision of the method.

Frequency - The frequency of collection and analysis of matrix specific QC samples should be based on the Data Quality Objectives (DQO) from the client's work plan. Due to the potentially many and unpredictable effects of sample matrix on the analysis, matrix specific QC results have little value in data assessment unless performed on site-specific matrices. Generally, the laboratory cannot effectively evaluate the needs for matrix specific QC at any particular site without client input; therefore, the frequency of matrix QC samples should be identified in the sampling plan. If samples are expected to contain the target analytes of concern, then the analysis of one matrix spike and a duplicate analysis of an unspiked field sample as an alternative to the MS/MSD pair may be appropriate.

Composition - If the test method does not specify the spiking compounds, the laboratory shall spike all reportable components in the MS/MSD. In cases where the components interfere with accurate assessment (such as simultaneously spiking chlordane, toxaphene and PCBs in Test method 608), other related analytes may be substituted for the multi-component analytes. Where the test method has an extremely long list of components (such as Test method 8270 or 6010) or components are incompatible, a representative number (10%) of the listed components may be used to control the test method. The selected components of each spiking mix shall represent all chemistries, elution patterns and masses and shall include permit specified analytes and other client requested components. Spiking levels should conform to method requirements. In the event that methods do not specify spiking levels, the laboratory should choose a spiking level between 20% and five times the native concentration of analyte in the sample.

Acceptance Criteria - Results from matrix specific QC analyses are primarily designed to assess the accuracy and precision of analytical results in a given matrix, and not laboratory performance. The results are expressed in percent recovery (%R) and Relative Percent Difference (RPD):

$$\%R = \frac{\text{Observed Value (MS)} - \text{Observed Value (native sample)}}{\text{Amount of Spike}} \times 100\%$$

For MS/MSD:

$$RPD = \frac{*\text{MS \%R} - \text{MSD \%R}*}{[(\text{MS \%R} + \text{MSD \%R})/2]} \times 100\%$$

For MD

$$RPD = \frac{*\text{MD Value} - \text{Native Sample Value}*}{[(\text{MD Value} + \text{Native Sample Value})/2]} \times 100\%$$

In general, if the matrix QC sample results are not within acceptance criteria, performance problems with matrix QC sample results may be related either to the specific sample matrix or to an inappropriate choice of extraction, cleanup, and determinative methods. This may also be due to a laboratory performance problem. A matrix related effect is indicated if the LCS data are within acceptance criteria but the matrix spike data are outside the acceptance criteria. The data assessment process should include consideration of all available batch QC and matrix specific QC sample results.

Suggested acceptance criteria for matrix specific QC samples are provided in some EPA methods. However, these criteria generally do not suffice for determining acceptable levels of accuracy and precision in a specific site matrix. The data user should be called upon to determine DQOs and decision making processes to assess the matrix specific QC results. Two possible alternative

procedures for selecting matrix specific QC sample acceptance criteria include the process described for LCS samples, and predetermination of data usability windows using a traditional data validation process. The latter involves pre-selection of windows specific for sample matrix, test, and test parameter.

~~2) Matrix Spikes (MS) -Shall be performed at a frequency of one in 20 samples per matrix type per sample extraction or preparation method except for analytes for which spiking solutions are not available such as, total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, odor, temperature, dissolved oxygen or turbidity. The selected sample(s) shall be rotated among client samples so that various matrix problems may be noted and/or addressed. Poor performance in a matrix spike may indicate a problem with the sample composition and shall be reported to the client whose sample was used for the spike.~~

3) Surrogates - Surrogate compounds must be added to all samples, standards, and blanks for all organic chromatography test methods except when the matrix precludes its use or when a suitable surrogate is not available. Surrogate recovery data from individual samples are compared to surrogate recovery acceptance criteria specified in methods. As with matrix specific QC results, surrogate recoveries are used primarily to assess data quality and not laboratory performance.

~~Surrogate compounds must be added to all samples, standards, and blanks, for all organic chromatography methods except when the matrix precludes its use or when a surrogate is not available. Poor surrogate recovery may indicate a problem with the sample composition and shall be reported to the client whose sample produced the poor recovery.~~

~~4) If the mandated or requested test method does not specify the spiking components, the laboratory shall spike all reportable components to be reported in the Laboratory Control Sample and Matrix Spike. However, in cases where the components interfere with accurate assessment (such as simultaneously spiking chlordane, toxaphene and PCBs in Method 608), the test method has an extremely long list of components or components are incompatible, a representative number (at a minimum 10%) of the listed components may be used to control the test method. The selected components of each spiking mix shall represent all chemistries, elution patterns and masses, permit specified analytes and other client requested components. However, the laboratory shall ensure that all reported components are used in the spike mixture within a two-year time period.~~

~~**D. 1.2 Analytical Variability/Reproducibility**~~

~~Matrix Spike Duplicates (MSDs) or Laboratory Duplicates -Shall be analyzed at a minimum of 1 in 20 samples per matrix type per sample extraction or preparation method. The laboratory shall document their procedure to select the use of appropriate type of duplicate. The selected sample(s) shall be rotated among client samples so that various matrix problems may be noted and/or addressed. Poor performance in the duplicates may indicate a problem with the sample composition and shall be reported to the client whose sample was used for the duplicate.~~

Attachment D

Attachment 2

THE APPROPRIATE USE OF MATRIX-SPECIFIC QUALITY CONTROL SAMPLES

Essential Data Assessment Tools for Environmental Analyses

Prepared By:
ELAB Quality Control Sample Subcommittee

Members:
Harry Gearhart, DuPont Engineering
Deborah Loring, STL Laboratories
Jerry Parr, Catalyst Information Resources
Kim Watson, STL Laboratories

For many years there has been confusion in the environmental community over the respective functions of **laboratory** quality control (QC) samples and those QC samples used for other purposes, defined in this document as **matrix-specific** (QC) samples (Carlberg). Unfortunately, this confusion has been compounded by some of the language in Appendix D.1 of Chapter 5 of the NELAC standards. The primary function of **laboratory** QC samples generated in the laboratory, such as the LCS and the method blank, should be to demonstrate that the laboratory is performing the method effectively at a particular point in time. In contrast, the primary function of the **matrix-specific** QC samples, such as surrogate spikes, matrix spikes, matrix duplicates, and field blanks should be to demonstrate how effective the method was when applied to the matrix at a particular site (Parr). This distinction does not exist in Appendix D.1.

While the analysis of laboratory QC samples can be considered an essential requirement for a quality system, and thus should be evaluated as part of a laboratory accreditation program, requirements to analyze matrix-specific QC samples should not be linked to accreditation requirements. Although these samples provide a valuable tool to assess the quality of environmental data, their use should be based on data user needs; as part of laboratory accreditation, laboratories need to demonstrate their ability to perform these analyses, when required by their customers.

Control of the analytical process is maintained using the batch principle, and a number of different batches may be identified. These include the sampling batch (a group of samples collected together), the preparation batch (a group of samples prepared together), and the analysis batch (a group of samples analyzed together). These latter two terms have been appropriately defined in the NELAC glossary. It is important to note that many laboratories combine samples collected from various sites into one preparation or analysis batch. Any given sampling batch may, or may not, include matrix-specific QC samples.

As noted in Appendix D.1, a method blank and LCS must be processed with each extraction batch. These samples are used to evaluate and control laboratory performance and are appropriate. However, Appendix D.1 also requires that the laboratory analyze matrix-specific QC samples as well. This requirement leads directly to two problems. The first is that the matrix QC results then tend to be used for laboratory control rather than evaluation of the site matrix effect on the analytical process. The second, much more serious issue, is that site investigators do not define the appropriate level of matrix-specific QC analyses since they know that the laboratory must perform some type of generic approach. This saves the site investigator money but has a very detrimental effect on overall data quality since the matrix-specific QC that the laboratory performs and reports will many times be on samples from a completely unrelated site.

Attachment D

As shown in Attachment 3, various matrix-specific QC samples have been defined (Wentworth). Only two of these QC samples, matrix spikes, and matrix spike duplicates (MS/MSD) and surrogate spikes (SS) are included in the Appendix D.1 requirements. The discussion below focuses only on MS/MSD analyses, as the requirements in NELAC for these samples are the most onerous. The suggested revisions to Appendix D include changes related to other types of matrix-specific QC samples as well.

WHAT DO MS/MSD RESULTS SHOW?

MS/MSD results are used to estimate the accuracy and precision of a measurement (i.e., the uncertainty in the measurement) for the sample which was spiked. If related samples from the site have similar physical and chemical characteristics, the MS results may, with caution, be used to extrapolate the expected uncertainty of the measurement to these other samples. The percent recovery is calculated for the MS/MSD, and the mean recovery can be used to estimate accuracy of the method on the site matrix. The Relative Percent Difference (RPD) is calculated for the MS/MSD, and can be used to estimate the precision of the method on the site matrix.

Some site matrices can show a significant bias. For example, in samples with high organic content, MS/MSD recoveries can often be significantly low (<50%) for organics. A low bias evident in the MS/MSD can often be extended to other samples at the site that are of a similar matrix. In this specific case, it would be appropriate to flag data from samples of that same matrix type at that site as being biased low, recognizing that target analytes reported at that site are likely to be underestimated. This information is crucial in risk assessment. Where contaminants of concern are detected at a site and are close to action levels, knowing that the data is biased low allows the data user to make responsible decisions with regards to actions taken based on the known bias of data close to action levels. Alternatively, if it is critical to obtain more accurate results, another more accurate method may be more appropriate.

Some site matrices can show a high bias. For example, highly complex organic matrices subjected to GC/ECD analyses for Pesticides, even with appropriate clean-up measures, can show a high bias, evident in MS/MSD recoveries. If this is the case, and target analytes detected at the site are close to or above action levels, it may be valuable to investigate the use of an analytical procedure less likely to be subject to these interferences, such as GC/MS.

CAN MS/MSD DATA BE EXTRAPOLATED TO OTHER SAMPLES AT THE SAME SITE?

Extrapolating the results of the MS/MSD to other samples at a given site should be performed carefully. However, it can be done in some cases, and assignment of qualifiers to indicate the measurement uncertainty is possible and appropriate and often performed as part of data assessment. Physical characteristics, such as particle size, porosity, percent moisture, etc. can be evaluated. Visual inspection of the samples is also valuable. Inspection of raw analytical data, such as chromatograms is also useful in determination of bias and its extension to other samples at the site. If for example, other samples show relatively the same types, levels and patterns of contaminants and exhibit, in the case of organics analyses, similar surrogate recoveries, bias determination can be appropriately extended. Examination of the patterns and interferences in raw data, such as evaluation of chromatograms is helpful in assessing whether an MS/MSD bias can be extended to affect other samples at the site. There presently exists no appropriate mathematical model to correct results for bias based on MS/MSD results for samples other than those which were spiked. All of the above mentioned indicators, however, should be assessed, as it cannot be assumed that all samples at one site are of a “similar” matrix.

Attachment D

HOW DO THE RESULTS OF THE MS/MSD REFLECT LABORATORY CONTROL?

The laboratory uses the results of the Laboratory Control Sample (LCS) and Method Blank to show that the method is in "control", i.e. that the laboratory processed the batch of samples within the expected performance of the method. These QC samples are analyzed with every laboratory batch. If the results of the LCS or method blank are out of control, the laboratory must take action, which most often will include reprocessing the entire batch of samples, but can include qualifying the results.

The MS/MSD results do not show whether the laboratory processed a batch within control guidelines. The laboratory generally does not, and should not take action (i.e. re-analyze MS/MSD, re-prepare and/or reanalyze batch, etc.) based on the MS/MSD results. The MS/MSD results do not show anything about the batch of samples with which they are processed. Laboratory batches may consist of samples from various sites, or samples of varying matrix composition within a given site. The MS/MSD results provide information about a specific sample only.

Re-processing a batch based on MS/MSD data, as well as re-preparing and re-running MS/MSD samples could effectively result in providing misleading data. If an MS/MSD sample was rerun repeatedly, until a run, by chance, came within control limits and that data was presented, this would be misleading, as a matrix effect present at a site would effectively be "masked" to the data user. Although this seems to be an unacceptable laboratory practice, there are some methods that actually require the laboratories reanalyze the MS/MSD, indicating that a failed MS/MSD indicate that the laboratory is out of control and the data in that laboratory batch cannot be reported for compliance purposes.

HOW OFTEN ARE MS/MSD SAMPLES ANALYZED?

The frequency that is presently required for MS/MSD samples varies with the regulatory program and with the specific methods within those programs, and there are often conflicts in the use and the frequency of MS/MSD samples. The most common interpretation for the hazardous waste program is that one set of MS/MSD or MS/MD be run per 20 samples. However, as discussed in Attachment 2, this frequency is not a requirement of the RCRA program. Furthermore, MSD sample analyses are not required for either NPDES compliance monitoring under the Clean Water Act nor drinking water compliance testing under the Safe Drinking Water Act.

To further complicate the issue, and as required by Appendix D, the frequency is often required to be implemented at the laboratory level, based on the samples received by the laboratory, independent of the data need, matrix, site, or customer. While the results from an MS/MSD analysis provides good information about the performance of the method on that sample, it provides only limited information about related samples, and probably little value for other samples from other sites.

The choice of which sample to run for MS/MSD is frequently left to the laboratory, and is often made based on which client has sent in additional volume, or, which sample appears to be the "cleanest." Because most laboratory clients know that the burden is on the laboratory to analyze an MS/MSD per 20 samples, and report those, they do not send in samples designated for MS/MSD analysis, perceiving it as a lab required laboratory QC activity. It can be difficult for a laboratory, particularly with water samples analyzed for organics, to get a sample with enough volume to perform the MS/MSD.

HOW ARE THE MS/MSD REPORTED?

Under the schemes as described above, MS/MSD data is inappropriately considered as "belonging" to a

specific laboratory batch and is generally required to be reported with all data generated from that laboratory batch (i.e. MS/MSD information is reported to all parties whose samples were prepared/analyzed in that particular batch). Many laboratory clients and/or regulatory agencies will reject data if not accompanied by this information.

HOW DOES THIS AFFECT ENVIRONMENTAL DATA QUALITY?

It is crucial that the laboratory not report MS/MSD data from a site other than the one from which the native sample was derived. If an MS/MSD is reported with all samples from the laboratory batch, and it shows no matrix effect, the data user may assume there is no bias in the results, even thought the MS/MSD is not derived from that data user's site. This assumption would be incorrect, and if there was, for example, a low bias, the decisions made based on these results could result in an underestimation of risk at the site. The EPA Office of Solid Waste recognized this and clarified it in the following statement: "The Agency further recommends that data users should be routinely provided with the MS/MSD results from only those QC samples associated with the field samples from the same site. (Cotsworth)"

WHAT IS THE APPROPRIATE FREQUENCY FOR MS/MSD?

The frequency of MS/MSD in relation to laboratory batches is irrelevant. If ongoing sampling is occurring at a specific site, the frequency should be determined based on that site matrix. The MS/MSD samples should be submitted to the laboratory at a frequency determined to be appropriate by the data user based on data quality objectives and what is known about the complexity of the site matrix. The MS/MSD data should only be associated with and reported to the client who submitted the samples. A default frequency of 5% (MS/MSD per 20 site samples) may be appropriate. However, for matrices such as drinking water, this may be unnecessary. For waste matrices, it might be advantageous to perform more frequent MS/MSD samples. The frequency of MS/MSD should reflect both the level of matrix effects expected and the data quality objectives applicable to the types of decisions that the data are supporting.

By applying the MS/MSD frequency to laboratory batches, the ability to use the MS/MSD results in the appropriate manner is lost. Laboratory batches comprise samples from various sites. The laboratory does not make decisions based on the MS/MSD results, however the data user should evaluate the effect of the site matrix on the accuracy and precision afforded by the method. The only way to allow the data user to make these decisions is by basing the MS/MSD frequency and application to site specific sample batches.

Another concern is that MS/MSD results, because they are being linked to laboratory batches, are being used solely (and incorrectly) to demonstrate laboratory accuracy and precision. MS/MSD results do not show this. However, since they are being routinely applied, associated and assessed in this manner, it is apparent that they are often used in the manner in which they were not intended. The goal of MS/MSD sample analyses should be to specifically to assess whether or not a bias exists due to a site matrix, and whether or not this should trigger either the use of an additional methodology (i.e. GC/MS instead of GC, Furnace AA instead of ICP), or whether the bias would warrant a concern that positively reported target analytes may be underestimated at a site and might be closer to health and environmental based action levels at a site than the data indicates.

In cases where the MS/MSD samples are site specific and applied at a site specific frequency, laboratories may have multiple MS/MSD samples in a particular batch, and may have some batches without any. Because MS/MSD results do not provide any laboratory control information, this is appropriate. All laboratory batches contain LCS and Method Blanks, which are used to document the

control of those batches. MS/MSD samples do not need to be extracted or prepared in the same batch as their associated field samples, because by default they will be prepared in laboratory batches with acceptable levels of accuracy and precision as evidenced by the LCS and Method blank. They may be related to samples from the same site that were run in various laboratory batches.

This is not unprecedented. The Superfund program, as well as most Department of Defense (DoD) programs, requires that MS/MSD be site specific and submitted to the laboratory at a designated frequency (Koran). The Superfund program is set up such that it does not matter what laboratory batch the MS/MSD is run in. In Superfund methods, the laboratory is instructed not to repeat MS/MSD analyses for perceived "outages". Most Sampling and Analysis Plans (SAP) and Quality Assurance Project Plans (QAPP) under DoD include site specific MS/MSD that are presumably assessed for that site only.

Many state programs require the laboratory batch approach to the frequency and reporting of MS/MSD samples, as do the present NELAC requirements in Appendix D.

MS/MSD results are an important measure of the performance of the method relative to the specific sample matrix of interest. The results from these tests are used to help establish the uncertainty of the measurement. While the MS/MSD results provide extremely useful information, this information is wholly site specific (whether the "site" is an effluent stream under NPDES, a drinking water sample under SDWA, or a waste sample under RCRA). Therefore, the appropriate frequency and the application of that frequency should be based on data quality needs rather than laboratory batches.

HOW ARE CONTROL LIMITS RELATED TO MS/MSD?

Because a laboratory does not control based on MS/MSD samples, the application of "control limits" should be defined as to their significance. This significance has not been adequately defined within the industry, and because of that, is often mis-applied to relate to laboratory control.

The most common approach is to set MS/MSD "control limits" at the limits derived from LCS samples. The limits used for LCS samples reflect the accuracy and precision that the laboratory should be able to achieve in a blank matrix, and would thus tend to represent a best case performance. Comparing the MS/MSD recoveries and RPDs to these limits would demonstrate where a matrix effect exists, i.e. that the laboratory method is accurate and precise within these limits, however, the site matrix shows a marked effect on the method such that the results are biased or imprecise.

Once that is understood, there is a second step in the evaluation process. LCS Control limits simply show how accurately and precisely a laboratory can perform a method with no matrix effects. However, they do not necessarily reflect how accurate and precise the data user needs the data to be in order to make an effective decision based on that data. This can be illustrated using the following example:

If a laboratory is running samples with relatively high salinity by ICP, MS/MSD results may show a high or low bias for selenium and lead, due to interferences associated with the sample matrix. There also may be problems with accuracy and precision seen in the high level analytes like sodium and calcium. LCS ranges for all of these analytes are quite narrow, as ICP analyses are quite accurate and precise, particularly in a blank matrix. Accuracy ranges of 90-110% are common.

Once the data user notes that there are matrix effects based on the results of the MS/MSD, the significance of this should be assessed. A significantly low bias in a lead or selenium result may be of concern at a site due to the health and environmental impact of low levels of those analytes. However, the

fact that sodium or calcium are, for example, slightly outside of the "control limits" of 90-100%, should cause little concern on the part of the data user, and no action should be necessary.

WHAT ARE THE RESPONSIBILITIES OF A LABORATORY IN EVALUATING MS/MSD RESULTS?

The requirement to perform MS/MSD sample analyses must arise from the data user and not the laboratory. The laboratory must however have procedures for performing these analyses, including:
tracking, managing and reporting MS/MSD analyses,
spiking appropriate analytes at appropriate concentrations,
calculating recoveries, and
evaluating the results for any laboratory performance problems.

These responsibilities would be appropriate items for evaluation under NELAC.

Attachment D

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Attachment D

Attachment 3

BACKGROUND MATERIAL

[Excerpts from EPA OSWER memo, Clarification Regarding Use of SW-846 Methods, August 7, 1998]

Item 4 - The Appropriate Use of Matrix Spike Results

Section 8.5 of Method 8000B recommends that a matrix spike (MS) and matrix spike duplicate (MSD) pair be analyzed with each batch of up to 20 samples. The MS/MSD results are an important measure of the performance of the method relative to the specific sample matrix of interest. The Agency believes that such a demonstration is an important aspect of an overall quality assurance program, and is particularly important for the RCRA program, where a wide range of different matrices are subject to regulation.

The 1 per 20 (5%) frequency is a default value that has been used in many EPA programs for many years. The Agency believes that a default frequency is needed to preclude some laboratories from deciding that no MS/MSD results need to be provided at all. However, the Agency also recognizes that other frequencies may be appropriate under other circumstances. For example, in the case of a long-term monitoring project involving a small number of analyses of a sample matrix that does not change, it should not be necessary to prove that the method applies to the matrix each time that samples are collected and analyzed.

To that end, the Agency recommends that, if another frequency for the MS/MSD analyses is chosen, that it be clearly documented in a sampling and analysis plan that is reviewed and approved by the relevant regulatory authority.

The Agency also is aware that some clients do not provide laboratories with additional volume of sample from which to prepare the MS/MSD aliquots. In some cases, the problem is an oversight on the part of the samplers. It may also be due to difficulties in obtaining sufficient volume, such as from a poorly producing groundwater well. However, in other instances, the client simply may be assuming that the laboratory will prepare the MS/MSD from another sample prepared at the same time. Unfortunately, this latter situation can result in the provision of MS/MSD results from a matrix that is only marginally related to the samples in question.

Due to the importance of the relationship between the matrices of the MS/MSD and the field samples, the Agency stresses that an MS/MSD pair (or a spiked sample and a duplicate sample) should be prepared from additional volumes of the material collected from the site in question. Each MS/MSD will require that additional sample volume from the site be provided to the laboratory by the field sampling personnel. The Agency further recommends that data users should be routinely provided with the MS/MSD results from *only* those QC samples associated with the field samples from the same site.

Finally, the Agency is aware of some persistent misunderstandings about the intended role of the MS/MSD analyses. The Agency stresses that the *primary* purpose of these QC analyses is to establish the applicability of the overall analytical approach (e.g., preparative, cleanup, and determinative methods) to the specific sample matrix from the site of interest. Unfortunately, some may believe that the MS/MSD results can and should *routinely* be used to evaluate performance of an individual laboratory. The Agency stresses that such use is *not* the Agency's intent in specifying that MS/MSD analyses be performed at a 5% frequency. The Agency specifically included a discussion of the use of a laboratory control sample (LCS) in Method 8000B, as one tool that should be used to evaluate laboratory performance. Section 8.5.5 of Method

8000B addresses the use of LCS results in conjunction with MS/MSD results to separate issues of laboratory performance and "matrix effects."

The Agency does believe that consistent *trends* in MS/MSD results can be somewhat useful in evaluating laboratory performance, as are trends in surrogate recoveries, LCS recoveries, and other QC data. However, the appropriate use of a *single* set of MS/MSD results is to evaluate *method* performance in the matrix of interest, not *laboratory* performance.

[Excerpts from the Corps of Engineers "Shell" Document, 23 NOV 1998.]

10.0 Laboratory Quality Control Procedures.

Laboratory overall method performance shall be monitored by the inclusion of various internal quality control checks which allow an evaluation of method control (batch QC), and the effect of the sample matrix on the data being generated (matrix-specific QC). Batch QC is based on the analysis of a laboratory control sample to generate accuracy (precision and bias) data and method blank data to assess the potential for cross contamination. Matrix-specific QC shall be based on the use of an actual environmental sample for precision and bias determinations from the analysis of matrix spikes, matrix spike duplicates, matrix duplicates, and surrogate spikes, etc. Site-specific PE samples could also be used, if available. The overall quality objectives are to implement procedures for laboratory analysis and reporting of data that are indicative of the degree of quality consistent with their intended use. Method quality objectives, given as QC sample acceptance limits and ranges may be default values established within this guidance, or may be based upon project DQOs. Laboratory generated control ranges are also used for an internal evaluation of method performance and control. Variances from any of these target ranges, would result in the implementation of appropriate corrective measures and an assessment of the impact on the usability of the data in the decision making process.

10.1 Sample Batching. The basic unit for application of laboratory quality control is the batch. Samples shall be prepared, analyzed, and reported in batches and be traceable to their respective batches. Batch sizes are normally limited to twenty field samples of a similar matrix but can exceed this by incorporating additional QC samples. Each batch shall be uniquely identified within the laboratory. Samples prepared together would normally be analyzed together on a single instrument. Samples taken from the same site would normally be grouped together for batching purposes within the constraints imposed by the method holding times. However, laboratories may find it necessary to group multiple clients samples into a single batch. Under these circumstances, additional batch QC samples may be needed that evaluate the effect of the matrix from each site on method performance. Field QC samples, i.e., trip blanks, rinsates, etc., shall not knowingly be used for batch QC purposes.

10.1.1 Preparation Batch. The preparation batch shall be defined as samples of the same or similar matrix that is prepared together by the same person, or group of people within the same time period or within limited continuous time periods, which follow the same method, using the same type of equipment and same lots of reagents. The laboratory shall have sufficient quantities of extraction/digestion labware to meet these requirements. Each preparation batch shall contain the requisite number and type of calibration solutions, blanks, quality control samples, and regular analytical samples as defined by the analytical method. These requirements shall be completely defined in the laboratory SOPs and are summarized in part in the following sections. The use of clean-up methods would be included as part of the preparation batch. All field and batch specific QC samples within the batch should be subjected to all preparatory and clean-up procedures employed.

10.1.2 Analysis Sequence. The analysis sequence or instrument run sequence shall be defined as samples that are analyzed together within the same time period or in continuous time periods on one instrument under the control of one continuing calibration verification. Analysis sequences would be bracketed by the appropriate continuing calibration verification standards and other QC samples as defined by the analytical method. In general, if an instrument is not used for periods of time or shut down (e.g., overnight, etc.), then a new analysis sequence shall be initiated. Each analysis sequence shall contain the requisite number and type of calibration solutions, quality control samples, and regular analytical samples as defined by the analytical method. These requirements shall be completely defined in the laboratories SOPs and are summarized in part in the following sections.

For samples that are purged and then analyzed immediately, the preparation batch and analysis sequences are combined. For this situation, the batch would normally be defined by the loading of samples into the various purge tubes. This definition has been interpreted differently however. For instance, the loading of purge tubes may be performed all at one time, or may continue throughout the day. In order to ensure ambient environmental conditions throughout the potential loading process, USACE requires a minimum of an MB run every four (4) hours, or twice a day when samples are loaded throughout the day.

10.2 Preparation Batch QC Samples. A summary of the minimum required QC samples for each preparation batch are as follows. All calibrations and QC samples analyzed shall be uniquely identified and traceable to that unique sample preparation batch. Additional QC samples may be required for other batch types based upon project DQOs.

10.2.1 Method Blank. Method blanks are analyzed to assess background interference or contamination that exists in the analytical system that might lead to the reporting of elevated concentration levels or false positive data. The method blank is defined as an interference-free blank matrix similar to the sample matrix to which all reagents are added in the same volumes or proportions as used in sample preparation and carried through the complete sample preparation, cleanup, and determinative procedures. For aqueous analyses, analyte-free reagent water would typically be used. For soil analyses, a purified solid matrix (e.g., sand) would typically be used, except for metals analyses. The results of the method blank analysis are evaluated, in conjunction with other QC information, to determine the acceptability of the data generated for that batch of samples. Refer to 11.4.1 for method quality objectives/corrective action scenarios for the MB. Sample results shall not be corrected for blank contamination.

10.2.2 Laboratory Control Sample. The LCS is analyzed to assess general method performance by the ability of the laboratory to successfully recover the target analytes from a control matrix. The LCS is similar in composition to the method blank. For aqueous analyses use analyte-free reagent water. For soil analyses, a purified solid matrix (e.g., Ottawa sand, sodium sulfate, or other purified solid) would typically be used. However, due to the difficulty in obtaining a solid matrix which is metals-free, analyte-free reagent water is taken through the appropriate digestion procedures for metals analyses. The LCS is spiked with all single-component target analytes before it is carried through the preparation, cleanup, and determinative procedures. A subset of the (single-component) target analytes containing the specific analytes of interest can be substituted for the full list of target analytes if specified in project-specific contracts or workplans. When multi-component target analytes are reported, a separate LCS may be necessary if specified by project documents. For Method 8082, the LCS must be spiked with at least one PCB (e.g., 1016/1260 mixture), any project-specified PCBs, or all congeners to support the LCS evaluation. The use of solid standard reference materials (SRMs) as the LCS is discouraged for they do not typically include all target analytes, and the acceptance limits associated with them are wide -- due to the heterogeneity of the spiked matrix. Suggest instead the use of an interference-free matrix (e.g., purified solid, or sodium sulfate). When samples are not subjected to a separate preparatory procedure

(i.e., purge and trap VOC analyses, or aqueous Hg analysis), the CCV may be used as the LCS, provided the CCV acceptance limits are used for evaluation. The spiking levels for the LCS would normally be set at the project-specific action limits assuming that the low standard used for the initial calibration was below this limit. If the low standard used was at this limit or if the site action levels were unknown, then the spiking levels would be set between the low and mid-level standards. The results of the LCS are evaluated, in conjunction with other QC information, to determine the acceptability of the data generated for that batch of samples. Refer to 11.4.2 for method quality objectives/corrective action scenarios for the LCS. The laboratory shall also maintain control charts, or tables for these samples to monitor the precision and bias for the method as outlined in 4.7.2. The precision may be evaluated by comparing the results of the LCS from batch to batch, or by duplicate LCSs. Duplicate LCSs within the same batch are not required, but recommended by the USACE.

10.2.3 Matrix Spikes. The matrix spike (MS) is used to assess the performance of the method as applied to a particular project matrix. A MS is an environmental sample to which known concentrations of certain target analytes have been added before sample manipulation from the preparation, cleanup, and determinative procedures have been implemented. Reference project-specific documents for the contaminants of concern, guidance presented below, or the preparatory and determinative methods to determine target analytes to include within the MS spiking solution. If no information is available, include all target analytes within the MS. The spike concentrations of the target analytes would normally be set at the same level as the LCS. If target analytes were known to be present in samples from a given site, then the spiking level should be adjusted to a concentration that is approximately two to four times the concentrations of the original target analytes. For solid samples, care should be taken to ensure that the original field sample is properly divided into homogeneous fractions when allowed by the method. Aqueous samples require the submittal of an additional sample for several chemical parameters, especially organic analyses. Therefore, the sample to be used for the MS should be based on project-specific DQOs and specified in the field to ensure that sufficient sample is available to perform the test. From the laboratory perspective, preparation batches require MS frequency at one per preparation batch. The merging of these MS frequencies is often difficult for the laboratory to implement. For instance, batches consisting of samples from multiple sites may require additional MSs to meet project requirements of evaluating the samples within the batch. For a MS from one site cannot be used to evaluate the matrix effects on samples from other sites. Projects must consider the method(s) employed, previous knowledge of the matrix, and other matrix-specific QC samples to help decide an appropriate frequency for MSs for a given project. As a consequence, a MS may not be included with each shipment of samples submitted to the laboratory. Communication between project and laboratory personnel is essential. The results of the MS are evaluated, in conjunction with other QC information, to determine the effect of the matrix on the bias of the analysis. Refer to 11.4.3 for method quality objectives/corrective action scenarios for the MS. When critical decisions are based on the MS sample recoveries, control charts could be maintained for these samples to monitor the bias of the method for each particular matrix. Sample results shall not be corrected for MS QC excursions.

10.2.3.1 Method 6010. Unless superseded by project DQOs, it is not necessary to perform matrix spikes for Na, K, Ca, and Mg for aqueous samples; or Na, K, Ca, Mg, Fe, Mn, and Al for soil samples. The native concentrations of these low-toxicity metals are usually relatively high.

10.2.3.2 Method 8081. The MS should be prepared all single-component pesticides. Multi-component pesticides need not be included within the MS, unless required by project DQOs.

10.2.4 Matrix Duplicates or Matrix Spike Duplicates. The matrix duplicate (MD) or matrix spike duplicate (MSD) is used to assess the performance of the method as applied to a particular matrix and to

provide information on the homogeneity of the matrix. An MSD is a duplicate of the MS as previously described. A MD is an environmental sample that is either divided into two separate aliquots by the laboratory, or requires the submittal of an additional sample. When applicable, care should be taken to ensure that the sample is properly divided into homogeneous fractions. Both the MD and MSD are carried through the complete sample preparation, cleanup, and determinative procedures. The requirements for the frequency of MDs or MSDs would normally be specified in the project-specific DQOs. The normal use of these QC samples would follow the same requirements as described for the MS. In the absence of project-specific DQOs, a MD would normally be included with each preparation batch of samples processed where target analytes were expected to be present (e.g., inorganic methods). An MSD would normally be included with each preparation batch of samples processed where target analytes were not expected to be present (e.g., organic methods). The results of the MD or MSD are evaluated, in conjunction with other QC information, to determine the effect of the matrix on the precision of the analysis. Refer to 11.4.4 for method quality objectives/corrective action scenarios for the MD or MSD. Control charts can be maintained for these samples to monitor the precision of the method for each particular matrix if required by the project.

10.2.5 Surrogates. Surrogates are analyzed to assess the ability of the method to successfully recover these specific non-target analytes from an actual matrix. Surrogates are organic compounds that are similar to the analytes of interest in chemical behavior, but are not normally found in environmental samples. Surrogates to use are identified within the determinative methods. Other compounds may be chosen and used as surrogates, depending on the analysis requirements, whether they are representative of the compounds being analyzed, and whether they cover the chromatographic range of interest. These compounds should be spiked into all samples and accompanying QC samples requiring GC, LC, or GC/MS analysis prior to any sample manipulation. As a result, the surrogates are used in much the same way that MSs are used, but cannot replace the function of the MS. The results of the surrogates are evaluated, in conjunction with other QC information, to determine the effect of the matrix on the bias of the individual sample determinations. Refer to 11.4.5 for method quality objectives/corrective action scenarios for surrogates. Control charts, or tables, shall be maintained for surrogates contained within the LCS or MB to monitor the accuracy of the method for each particular matrix. Sample results shall not be corrected for surrogate excursions.

Explosives' analysis by Method 8330 is an exception, in that the surrogate used is actually a target analyte. Care should be exercised by the laboratory with the choice of surrogate used, for the potential remains for coelution with target analytes present within the samples. If 3,4-DNT is used as the surrogate, it must not coelute with TNT. If it is not possible to obtain adequate resolution between 3,4-DNT and TNT, another surrogate should be chosen (e.g., 1,2-DNB).

10.2.6 Standard Reference Materials. The laboratory is encouraged to analyze additional natural matrix standard reference materials (SRMs) and participate in external performance evaluation (PE) programs.

10.3 Analysis Sequence QC Samples. Certain inorganic analyses (metals by ICP and GFAA) incorporate the following additional QC samples to assess method performance without the influence of the preparatory procedures.

10.3.1 Post-Digestion Spikes (PDS). PDSs are incorporated into an analytical sequence to assess matrix effects based upon (1) the occurrence of new and unusual matrices included within the batch, or (2) contingency analysis based upon serial dilution (SD) or matrix spike (MS) failures. Duplicate injections of each environmental sample may be avoided if a post-digestion spike (PDS) is performed for each sample. PDSs are prepared by the addition of the primary source standard to the digestate for the same metals

and at approximately the same concentration as is used for the MS. Refer to 11.4.6 for method quality objectives/corrective action scenarios for PDSs.

10.3.2. Serial Dilutions (SD). A 5X (1:4) serial dilution test may be performed for an analyte to evaluate matrix interference if the analyte concentration in the original (undiluted) sample is at least 50 times the MDL. SD - Matrix effects are suspected if the RPD between the undiluted and diluted result > 10%. If this criterion is not met, further confirmation of the interference via implementation of PDS is necessary when matrix interference is suspected, and the calculation of the result through the use of MSA when matrix interference is suspected/confirmed.

NOTE: When serial dilutions are used to address matrix interference, only best diluted results (i.e., the lowest dilution which yielded acceptable results) need be reported. However, the reported result must be qualified (i.e., D-flag) and the dilution factor specified. The associated MQLs or MRLs must also be adjusted based on the dilution factor.

[Excerpts from EPA QA/G-8]

collocated samples — two or more portions collected at the same point in time and space so as to be considered identical. These samples are also known as field replicates and should be identified as such.

duplicate samples — two samples taken from and representative of the same population and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variance of the total method, including sampling and analysis. See also collocated sample. Duplicate samples may also be generated in the lab instead of collected in the field.

field (matrix) spike — a sample prepared at the sampling point (i. e., in the field) by adding a known mass of the target analyte to a specified amount of the sample. Field matrix spikes are used, for example, to determine the effect of the sample preservation, shipment, storage, and preparation on analyte recovery efficiency (the analytical bias).

field blank — a sample used to provide information about contaminants that may be introduced during sample collection, storage, and transport; a clean sample, carried to the sampling site, exposed to sampling conditions, returned to the laboratory, and treated as an environmental sample.

matrix spike — a sample prepared by adding a known mass or volume of a target analyte to a specified amount of matrix sample for which an independent estimate of the target analyte concentration is available. Spike samples are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

quality control (QC) sample — an uncontaminated sample matrix spiked with known amounts of analytes from a source independent of the calibration standards. Generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.